

Simple predictive relations, fugacities, and enthalpies of dissociation for single guest clathrate hydrates in porous media

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Abstract

We present two sets of explicit relations for the equilibrium fugacities of single-guest gas hydrates. These relations can be applied whether the hydrate is dissociated under bulk conditions, or in porous media. The first set of presented relations explicitly shows the dependence of the equilibrium fugacity and the enthalpy of dissociation on classical statistical thermodynamic parameters. The second set of relations for the fugacity and enthalpy represent a very simple empirical form which can be used to calculate these quantities, without having to resort to the use of the full statistical thermodynamic model. It is hoped that these relations will prove useful in engineering or computational endeavors where the speed and/or ease of their use may be advantageous.

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1. Introduction

Gas hydrates are crystalline structures that belong to a group of solids known as clathrates, and which involve a lattice made up of hydrogen-bonded water molecules that form cavities, some of which are occupied by guest gas molecules. Gas hydrates form under low temperature–high pressure conditions, both above and below the freezing point of water. Under proper conditions, the lattice is stabilized by van der Waals forces through the occupation of specific cavities within the lattice by certain types of guest molecules. The type of guest molecule(s) present determines which of three known crystal structures the lattice assumes (Sloan, 1997).

Many of the hydrate deposits found in nature occur in permafrost regions or beneath deep oceans, where they are commonly found in sediment pores, where they may act as a cement holding the sediment together. Henry et al. (1999) and Clarke et al. (1999) have presented models, based on earlier statistical thermodynamic models (van der Waals and Platteeuw, 1959), that allow the prediction of equilibrium pressures when the porous medium contains a single size

pore. In the approaches of Henry et al. (1999) and Clarke et al. (1999) a term resulting from the capillary pressure was added to the equation of van der Waals and Platteeuw to interpret data (Handa and Stupin, 1992) resulting from experiments with a porous medium having a broad pore-size distribution.

On the basis of experimental data (see, for example, Sloan, 1997; Holder et al., 1988; Kamath, 1984; Parrish and Prausnitz, 1972), empirical relations for the equilibrium pressure of gas hydrates as a function of temperature have been presented in the literature for hydrate formation in the bulk. These empirical relations show excellent correlations with the experimental data. In a recent work (Wilder and Smith, 2002), the authors presented the derivation of the general form of these empirical relations for bulk hydrate formation starting with a standard statistical thermodynamic model, and showed how the physical model parameters affect the predicted equilibrium pressures. The derivation was shown to also be applicable to the case of hydrates in porous media.

In order for our previous derivation to be valid, the cages making up the hydrate structure must have relatively large occupancies. In addition, the approach was only applied to cases where the gas solubility in water was negligible (Wilder and Smith, 2002). The purpose of the present work is two fold. First, we present new relations for hydrates that have relatively small fractional occupancies, as well as for

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hydrates formed from gases with water solubilities that are not negligible. In both cases, the presented relations are derived from a standard statistical thermodynamic model for hydrate equilibria. Second, we show that even when the assumption of large fractional occupancy and/or negligible water solubility of the gas is not rigorously satisfied (such as in the case of carbon dioxide or hydrogen sulfide hydrate), the simple functional form found previously leads to a highly accurate empirical form whose ease of use may be desirable for engineering applications. In addition, the enthalpy of dissociation can be calculated from either set of relations with very small errors by means of the presented equations for the equilibrium fugacity.

2. Empirical fits to bulk hydrate data

Kamath (1984) noted that the equilibrium pressures for hydrates with a single guest component are well fit by simple relations of the form

$$\ln(P_{\text{eq}}) = A + \frac{B}{T}. \quad (1)$$

In Eq. (1) P_{eq} is the equilibrium pressure of the guest, T is the temperature, and A and B are fitted parameters. The apparent ability of equations of the form of Eq. (1) to fit experimental data for gas hydrates (see for example, Sloan, 1997; Holder et al., 1988; Kamath, 1984) suggests that an equation of this form might be derivable from the statistical thermodynamic equations used to predict hydrate formation. The ability to derive such relations from the full model was confirmed by work reported elsewhere (Wilder and Smith, 2002), as noted above. In the next section, we discuss the use of these previous results to hydrocarbon hydrates, as well as extensions applicable for hydrogen sulfide or carbon dioxide hydrate.

3. Explicit relations for hydrate equilibria involving thermodynamic parameters

Numerous authors have presented statistical thermodynamic models based on variations of the van der Waals–Platteeuw equation. Munck et al. (1988) used a previously developed model (Parrish and Prausnitz, 1972) to obtain a single equation involving T_f and P_f (the temperature and pressure under which the hydrate forms) that can be used to predict hydrate formation conditions. In the case of hydrates formed from single-component gases, this equation takes the form

$$\begin{aligned} \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{R\bar{T}} dP \\ - \ln(\gamma_w X_w) + \sum_i \eta_i \ln(1 - Y_i) = 0. \end{aligned} \quad (2)$$

In Eq. (2), $\bar{T} = (T_0 + T_f)/2$, T_0 is the temperature of the standard reference state ($T = 273.15$ K, $P = 0$), $\Delta\mu_w^0$ is the

chemical potential difference between the empty hydrate lattice and pure water in the reference state, η_i is the ratio of the number of cavities of type i to the number of water molecules in the hydrate lattice, and Y_i denotes the probability of a cavity of type i being occupied by the guest molecule. The probability Y_i is given in terms of the fugacity of the hydrate guest (f) in the gaseous state (calculated using the Soave–Redlich–Kwong equation of state) and the Langmuir adsorption constant (C_i) by

$$Y_i = \frac{C_i f}{1 + C_i f}. \quad (3)$$

Additionally, $\Delta H_w = \Delta H_w^0 + \int_{T_0}^T \Delta C_p(T') dT'$, where ΔH_w^0 is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature, $\Delta C_p(T')$ is assumed constant (Munck et al., 1988) and equal to ΔC_p^0 (the reference heat capacity difference), and ΔV_w is the volume difference between the empty hydrate and pure water (at T_0), and is assumed constant. Also note that the values used for ΔC_p^0 , ΔH_w^0 , and ΔV_w depend on whether the equilibrium involves liquid or solid water. Munck et al. (1988) and Parrish and Prausnitz (1972) accounted for the temperature dependence of the Langmuir constants by using the functional form

$$C_i = \frac{A_i}{T} \exp(B_i/T), \quad (4)$$

where A_i and B_i are experimentally fit parameters, and are dependent on which guest molecule is present, as well as which hydrate structures is formed. The fourth term on the left-hand side of Eq. (2) is due to the affect of the gas solubility on the activity of the water, and involves the activity coefficient (γ_w) and the mole fraction of gas in the aqueous phase (X_w).

To describe hydrate formation in porous media, Eq. (2) must be modified to include the effect of the relevant interface on the activity of the water. After making the necessary modifications in the region where the equilibria involve liquid water, Eq. (2) becomes (Henry et al., 1999)

$$\begin{aligned} \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{R\bar{T}} dP \\ - \ln(\gamma_w X_w) + \sum_i \eta_i \ln(1 - Y_i) \\ + V_L \frac{2 \cos(\theta) \sigma}{RT_f r} = 0. \end{aligned} \quad (5)$$

In Eq. (5), V_L is the molar volume of water in the aqueous phase, θ is the contact angle between the aqueous phase and the hydrate, σ is the surface tension of the interface between the hydrate and the aqueous phase, and r is the radius of a pore in the porous medium. Because the solubility of most guests in water is small, these parameters are approximated by their values for pure water. Eq. (5) can be used for all temperatures, though some of the parameters will

have different values depending on whether the temperature is above or below the quadruple point (the point at which water, ice, hydrate, and free gas are all in equilibrium) in the corresponding pore of radius r . Below this temperature one recovers the same equation as that given above for the bulk, since our model assumes there are no surface effects between ice and hydrate (Wilder et al., 2001), in accordance with recent experimental results (Zhang et al., 2002).

In this work, in addition to predictions of the natural logarithm of the equilibrium fugacity, we are also interested in the enthalpy of dissociation of the hydrates. If we make the assumption that we have a hypothetical porous medium in which all of the pores are the same size (having a radius given by r), then the relation given by Handa and Stupin (1992) relating the gas fugacity to the enthalpy of dissociation

$$\frac{d(\ln(f))}{d(1/T)} = -\Delta H/R, \quad (6)$$

would still be as valid as it is for the case of bulk hydrates. Eq. (6) will be used along with relations for the equilibrium fugacity to determine the enthalpy of dissociation for single guest hydrates.

3.1. Relations for gases having low water solubilities and high fractional occupancies (methane, ethane, and propane)

For gas hydrates involving guests whose solubility in water is negligible, and whose fractional occupancies of the relevant cages are large, it has been reported that Eq. (2) led to an approximation for the logarithm of the equilibrium fugacity of the form (Wilder and Smith, 2002)

$$\ln f \approx \ln f^0 + \frac{\Delta V}{(\eta_s + \eta_l)RT} e^{\ln f^0}, \quad (7a)$$

where

$$\ln f_{\text{pore}}^0 \approx \frac{1}{\eta_s + \eta_l} \left\{ \left(\frac{\Delta \mu_w^0 - \Delta H_w^0}{RT_0} - \eta_s [\ln(A_s/T_0) - 1] - \eta_l [\ln(A_l/T_0) - 1] \right) + \left(\frac{\Delta H_w^0}{R} - \eta_s(T_0 + B_s) - \eta_l(T_0 + B_l) \right) \frac{1}{T_f} + \left(\frac{2V_L \cos(\theta)\sigma}{R} \right) \frac{1}{T_f r} \right\} \\ \approx \alpha + \frac{\beta}{T_f} + \frac{\gamma}{T_f r}. \quad (7b)$$

This equation should be valid for such hydrates as those formed from methane and ethane (both of which are sI hydrates), as well as for propane (an sII hydrate), all three of which have over 89% of each of the relevant cages occupied by a guest gas molecule (as calculated based on Eqs. (3) and (4) utilizing the parameters given by Munck et al. (1988)).

Eq. (7) can be used for hydrate equilibria involving either liquid water or ice, except that in the two cases different values of some of the statistical thermodynamic parameters must be used. Fig. 1 shows the results of using Eq. (7) along with the thermodynamic parameters given by

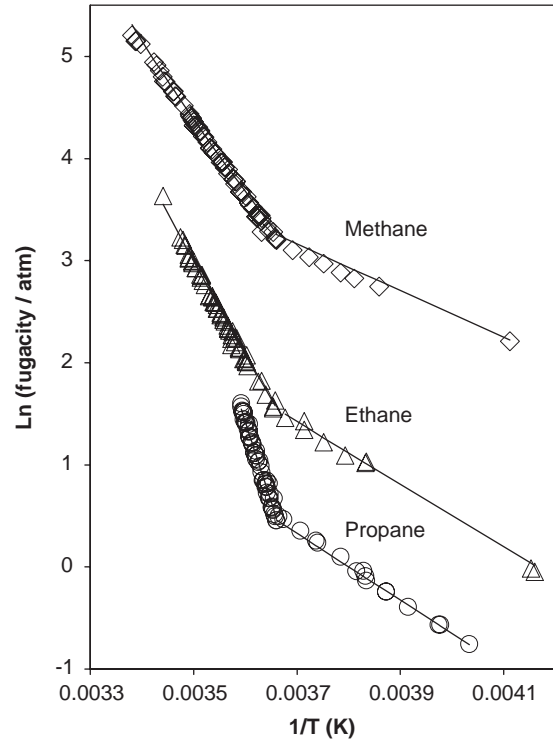


Fig. 1. Comparison of the predictions of Eq. (7) (solid traces) with experimental data (open symbols) for methane, ethane, and propane hydrates.

Munck et al. (1988) to predict the log of the hydrate equilibrium fugacity for bulk ($r \rightarrow \infty$) methane, ethane, or propane hydrate. We note that in the case of methane the temperature range is restricted to that shown to ensure that the methane is not supercritical.

The enthalpy of dissociation for hydrates meeting the criteria set out above can be calculated from Eq. (6) using the

form for the logarithm of the fugacity given by Eq. (7)

$$\Delta H \approx -R \left\{ \beta + \frac{\gamma}{r} + \frac{2\Delta V}{R(\eta_s + \eta_l)} \times \left[\left(\frac{T_f}{T_0 + T_f} \right)^2 + \frac{\beta + \frac{\gamma}{r}}{T_0 + T_f} \right] e^{\alpha + \beta/T_f + \gamma/T_f r} \right\}. \quad (8)$$

Various experimental values have been reported in the literature for the enthalpy of dissociation of bulk methane hydrate to liquid water at 273.15 K (ΔH_m^0). For example, this enthalpy of dissociation has been reported by Handa (1986) to have the value of 54.19 ± 0.28 kJ/mol. The use of Eq. (8) results in a value of 53.37 kJ/mol, a 1.5% difference. We note that Marshall et al. (1964) report a value within experimental error of that given by Eq. (8), namely 53.41 kJ/mol. For propane and ethane, Handa (1986) reports experimental values for ΔH_m^0 of 129.2 ± 0.4 and 71.80 ± 0.38 kJ/mol, respectively, while Eq. (8) yields 129.25 and 72.17 kJ/mole, both of which are within experimental error of these literature values. Clearly, Eqs. (7) and (8) yield accurate predictions of the logarithm of the equilibrium fugacity (see Fig. 1), as well as the enthalpy of dissociation for these hydrates. The quality of the agreement of the latter with experimental values is related to the validity of Eq. (6) given the good agreement of the experimental fugacities with those predicted by Eq. (7).

3.2. Relations for gases having low water solubilities and moderate fractional occupancies (hydrogen sulfide)

If one attempts to apply the approximation given above to a gas such as hydrogen sulfide, it is quickly observed that Eq. (7) results in predictions that differ from the full model by on the order of 5–10%. This discrepancy is due to the fractional occupation of the hydrate cages. While the gas hydrates discussed in the previous section had fractional occupancies on the order of 89% or larger, hydrogen sulfide hydrate has fractional occupancies of the small cages as low as 60% (based on Eq. (3)). A new approximation

$$f \approx \frac{\eta h_w \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{RT} + \frac{1}{h_w} \right) \right)}{2 \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{RT} + \frac{1-\eta}{2h_w} \right) \right)} \left(1 - \sqrt{1 - \frac{4 \left(a(T) - \frac{1}{\eta} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \right) \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{RT} + \frac{1-\eta}{2h_w} \right) \right)}{\eta h_w \left(\frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{RT} + \frac{1}{h_w} \right) - 1 \right)^2}} \right). \quad (10)$$

appropriate for such situations is derived in the appendix. As done by Munck et al. (1988), we shall ignore the solubility of hydrogen sulfide. Using this approximation and the method described in the appendix, the equilibrium gas fugacity for hydrogen sulfide hydrate is given by

$$f \approx \frac{C_s^{-\frac{\eta_s}{(\eta_s+\eta_l)}} C_l^{-\frac{\eta_l}{(\eta_s+\eta_l)}} \left(\frac{T_0}{T_f} \right)^{\frac{\Delta C_p^0}{R(\eta_s+\eta_l)}} \exp \left(\frac{\Delta H_w^0}{RT_f} + \left(\frac{\Delta H_w^0 - T_0 \Delta C_p^0}{R} \right) \left(\frac{1}{T_f} - \frac{1}{T_0} \right) + V_L \frac{2 \cos(\theta) \sigma}{RT_f r} \right) - \frac{1}{\eta} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right)}{1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \frac{\Delta V_w}{RT_f}}. \quad (9)$$

Fig. 2 shows the comparison of experimental results with the predictions of Eq. (9). Also presented in the appendix (Eqs. (A.9) and (A.10)) are relations which can be used to calculate the enthalpy of dissociation. Clearly, which such a close correspondence between the experimental and predicted fugacities, the enthalpy of dissociation (which depends on the

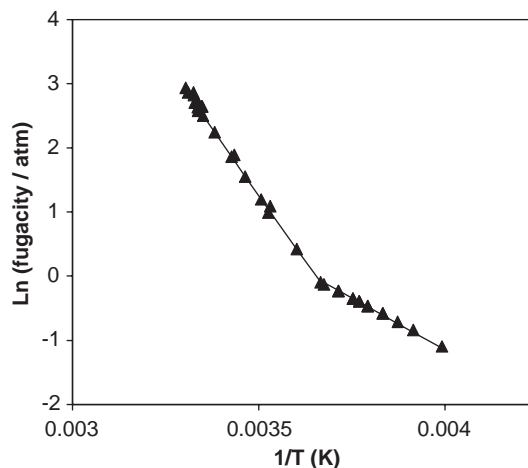


Fig. 2. Comparison of the predictions of Eq. (9) (solid trace) with experimental data (Sloan, 1997) (triangles) for hydrogen sulfide hydrate.

derivative of the curve shown in Fig. 2) calculated using Eqs. (9), (A.9), and (A.10) will also be accurate.

3.3. Relations for gases having moderate water solubilities and moderate fractional occupancies (carbon dioxide)

Due to the inclusion of the gas solubility in water, the relation for the equilibrium fugacity for carbon dioxide is more complicated than that of the other two cases given above. As discussed in the appendix, the inclusion of the gas solubility results in

Fig. 3 shows the predictions for equilibria involving liquid water (where Eq. (10) would be valid). For equilibria involving ice (in which case the gas solubility would be negligible), Eq. (9) could be used. As in the previous case, Eqs. (A.9) and (A.10) can be used in conjunction with

Eq. (10) to predict enthalpies of dissociation for carbon dioxide hydrate. Given the quality of the agreement between the experimental and predicted fugacities, one would again expect good agreement between the experimental and predicted enthalpies of dissociation.

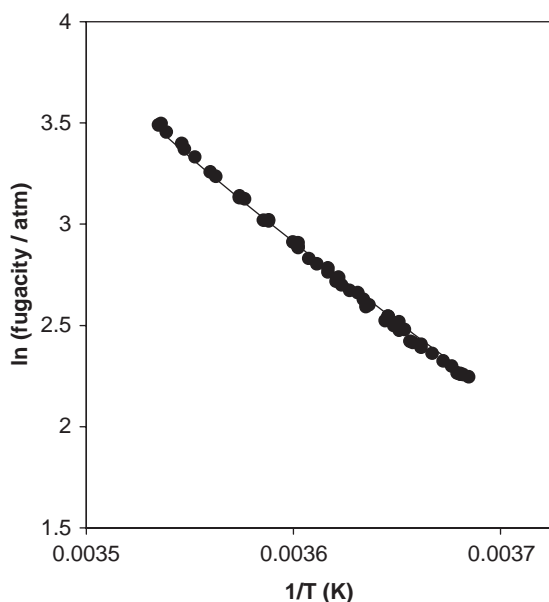


Fig. 3. Comparison of the predictions of Eq. (10) (solid trace) with experimental data (Sloan, 1997) (circles) for carbon dioxide hydrate.

4. New empirical relations for equilibrium fugacities and enthalpies

4.1. Prediction of equilibrium fugacities

Eqs. (7), (9), and (9) demonstrate the dependence of single guest equilibrium fugacities on statistical thermodynamic parameters. As noted in an earlier work, even though Eq. (7) is not valid except under conditions such that the gas solubility in water is negligible and the fractional cage occupancies are large, its functional form can be used to determine fitting parameters even for hydrates such as carbon dioxide. As an example of this, we now shall use the functional form

$$\ln f \approx a + \frac{b}{T_f} + c \ln(T_0/T_f) + \frac{e}{rT_f} + d \frac{\exp(a + \frac{b}{T_f} + c \ln(T_0/T_f) + \frac{e}{rT_f})}{T_f + T_0}, \quad (11)$$

which is a generalization of Eq. (7) (see Eqs. (12) and (14) of Wilder and Smith, 2002), and will demonstrate that fitting parameters a – e can be determined such that it gives excellent fits to the full model (Eq. (5)).

Shown in Table 1 are the results of fitting Eq. (11) to the predictions of what we will call the “sloan-based model” (SBM). This model, which is an analogue of Eq. (5), is based on the model of Sloan (1997) for bulk hydrates, suitably modified by addition of the capillary pressure term to allow it to predict equilibrium pressures in porous media. It uses the model parameters given by Sloan (1997) in Chapter 5, along with the Kihara potential used by Sloan (1997) (see Chapter 5) to obtain the appropriate Langmuir constants. Using Eq. (5), equilibrium pressures were calcu-

lated on a rectangular grid of $1/T$ and $1/rT_f$ values using ranges of r and T_f given by $2.5 \text{ nm} \leq r \leq 11 \text{ nm}$, and $255 \leq T_f \leq 270$. The equilibrium pressures were then converted to fugacities using the Soave–Redlich–Kwong equation of state (see, for example, Sloan, 1997 for a description of this and other suitable equations of state). The range in r was selected to reflect one which our experiments have shown to result in appreciable changes in the experimental equilibrium pressures for various single guest hydrates (Zhang et al., 2002; Smith et al., 2002, 2004; Seshadri et al., 2001) with respect to the bulk equilibrium pressure. Due to the depression of the freezing point of a liquid when confined in a small pore Clennell et al. (1999), the range of temperature selected here captures equilibria involving liquid water as well as ice for the range of pore sizes examined. In arriving at these results we have used the value of 0.0267 J/m^2 for the surface tension between hydrate and liquid water proposed by Henry et al. (1999). We have proposed that $\sigma \cos \theta$ is negligible for the hydrate–ice interface (Wilder et al., 2001; Zhang et al., 2002; Smith et al., 2002, 2004). This assumption has been recently verified by experiments involving ethane hydrate in silica gels with nominal pore radii in the range from 3 to 7.5 nm at temperatures below the quadruple point for the smallest hydrate containing pores (Uchida et al., 2002). This conclusion appears to also be supported by the data reported by Uchida et al. for methane hydrate in porous glass Seshadri et al. (2001), which show no pore size effect at sufficiently low temperatures. There are currently no experimental data that allow for the determination of whether $\sigma \cos \theta$ is small due to the value of the surface tension, or due to the smallness of the cosine of the wetting angle.

Fig. 4 shows the comparison of the full model (i.e., the analogue of Eq. (5) based on the model proposed by Sloan (1997)), with Eq. (11) using the parameter values given in Table 1 for methane hydrate. This figure shows the percent differences between the equilibrium fugacity predicted by the SBM and Eq. (11) projected onto the percent difference in equilibrium fugacity—temperature and percent difference in equilibrium fugacity—pore size planes. In addition, the maximum and average absolute percent differences are given in Table 2. Note that for methane, the maximum percent difference between the two predictions is approximately 0.1%.

The percent difference between predictions of Eq. (11) and the full model for bulk methane hydrate was found to always be less than 1.7%. It should be noted that these errors do not represent the best fit that could be obtained for the bulk data, but are rather the result of fitting to data from the rather narrow ranges of r and T of $2.5 \text{ nm} \leq r \leq 11 \text{ nm}$, and $255 \leq T_f \leq 270$, and then extrapolating to infinity for r , as well as to a range of temperatures that is approximately three times as large as the one used to arrive at the parameters. If, instead of starting with the pore data we fit Eq. (11) to the predictions of the SBM using the temperatures for which there are experimental data as the basis, we obtain parameter values of $a = 23.810$, $b = -6287.75$,

Table 1

Best fits to Eq. (11) for equilibria involving (a) the indicated hydrate structure (sI or sII), liquid water, and free gas and (b) the indicated hydrate structure (sI or sII), ice, and free gas for several single-component gas hydrates

Parameter	Methane (sI)	Ethane (sI)	Propane (sII)	Carbon dioxide (sI)	Hydrogen sulfide (sI)
(a) the indicated hydrate structure (sI or sII), liquid water, and free gas for several single-component gas hydrates					
<i>a</i>	−3.679	−4.413	−27.985	7.639	−2.440
<i>b</i>	1242.7	973.16	7087.0	−2079.1	52.977
<i>c</i>	−27.903	−34.455	−80.553	−16.949	−26.868
<i>d</i>	8.694	8.062	35.989	60.387	48.584
<i>e</i>	696.0	897.33	1964.64	748.87	703.99
(b) the indicated hydrate structure (sI or sII), ice, and free gas for several single-component gas hydrates					
<i>a</i>	6.740	8.673	18.692	7.923	7.737
<i>b</i>	−1579.1	−2589.7	−5765.1	−2137.9	−2721.4
<i>c</i>	−2.257	−1.305	13.898	−1.421	−0.9786
<i>d</i>	−14.911	−52.613	2323.7	−25.666	−182.24
<i>e</i>	N/A	N/A	N/A	N/A	N/A

Table 2

Percent differences between Eq. (11) and the SBM for several single-component gas hydrates

% Diff in Fugacity	Methane (sI)	Ethane (sI)	Propane (sII)	Carbon dioxide (sI)	Hydrogen sulfide (sI)
Max abs % diff (liq)	1.06E − 01	4.45E − 02	2.02E − 01	7.45E − 01	5.00E − 02
Ave abs % diff (liq)	2.28E − 02	8.45E − 03	1.79E − 02	1.18E − 01	9.10E − 03
Max abs % diff (ice)	6.95E − 05	1.89E − 04	6.05E − 04	6.46E − 05	6.15E − 05
Ave abs % diff (ice)	7.91E − 06	2.12E − 05	7.05E − 05	8.06E − 06	1.58E − 05

$c = 1.4638$ and $d = 29.1868$. When the results of Eq. (5) using these parameters are compared with the results from the SBM for the bulk, it is found that the maximum error in the prediction of the equilibrium fugacity is 0.28%, with the average error being 0.08%. However, when these parameters are then used in Eq. (11) and the value of e used to fit the model to the pore data, the maximum error rises to approximately 3% (at the smallest pore sizes and largest temperatures), with the average difference being 0.98%. As can be seen, better results are obtained by first fitting Eq. (11) to the pore data, and then extrapolating to the bulk, if one is interested in a single equation that can be used over the full ranges of temperature and pore size considered here. We note that the differences between the SBM and the predictions for the bulk using Eq. (11) based on the parameters in Table 1 are less than those between Sloan's model and the experimental data. These results clearly show that the functional form given by Eq. (11) can be applied to other models than the one from which it was derived (i.e., that used by Munck et al., 1988), and that the resulting predictions are valid over a wide range in temperature, as well as a range of pore size that encompasses scales on the order of nanometers up to infinity. While it would be preferable to have compared model predictions with experimental data for hydrate equilibrium pressures in porous media, there are no data which involve media containing a single pore size. As discussed in detail elsewhere (Wilder et al., 2001;

Smith et al., 2002), the presence of a distribution of pore sizes in the porous medium does not allow such direct comparisons between predictions and experimental results.

As noted above, the derivation of Eq. (11) presented elsewhere (Wilder and Smith, 2002) assumed that the solubility of the gas was negligible, and that the cage occupancies were high. We now turn to a case where this assumption is clearly incorrect, namely carbon dioxide hydrate. Due to the higher solubility of carbon dioxide in water (as compared with methane), the relative importance of the gas solubility is much greater in predictions of the equilibrium pressure (or fugacity). If one uses a standard model for the Langmuir constants such as that given by Sloan (1997), it is easily shown that for carbon dioxide hydrate the small cages in structure I carbon dioxide hydrate have a fractional occupancy that is around 75% over much of the bulk hydrate temperature range. This fractional filling is not large enough for all of the assumptions necessary for Eq. (11) to be explicitly derived from Eq. (5). Carbon dioxide hydrate thus represents a more serious challenge for the functional form presented in Eq. (11) than does that explored above for methane hydrates.

Table 1 gives the results of using the SBM to calculate equilibrium fugacities for carbon dioxide hydrate, and then fitting Eq. (11) to these predictions. The maximum and average errors between these two predictions are given in Table 2. Note that the maximum difference is less than 0.75%.

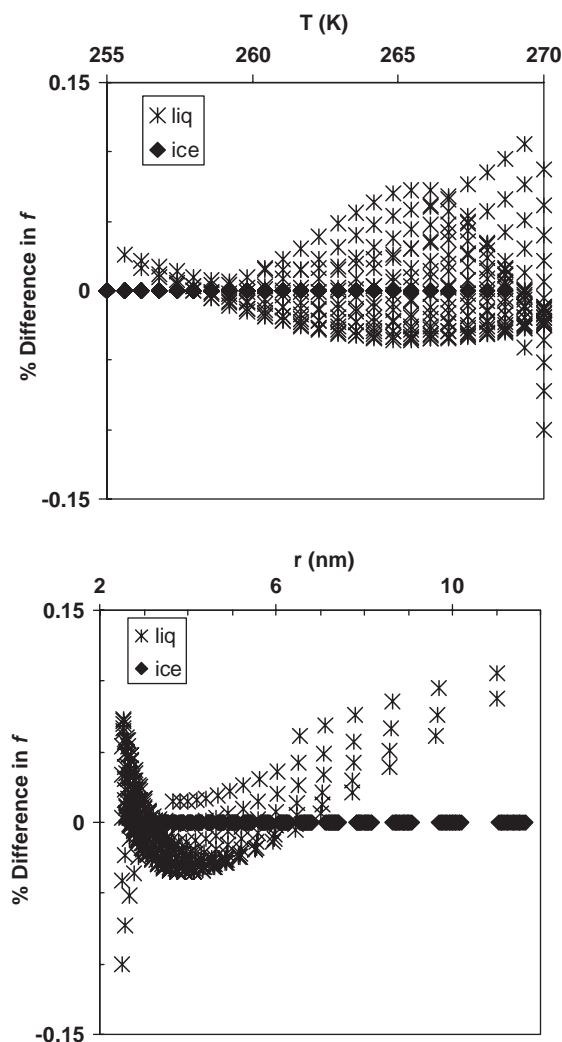


Fig. 4. Percent difference between predictions using Eq. (11) and those based on the SBM for methane hydrate over the indicated ranges of temperature and pore size.

Fig. 5 shows the errors in extrapolating Eq. (11) to make predictions concerning bulk hydrates. The maximum percent difference between the two predictions is less than 0.9%, and is again smaller than the difference between the predictions of the SBM and the experimental data. This case, which includes both a gas with significant solubility as well as occupancies that can range down to the 70% range demonstrates that even under these conditions the functional form given by Eq. (7) can be used with good results.

Tables 1 and 2 containing the fitting parameters for Eq. (11) and the errors in its use for all of the gas hydrates considered in this work.

4.2. Prediction of enthalpies of dissociation

Similar to Eq. (8), the use of Eq. (11) as our relation for $\ln f$ in Eq. (6) leads to the prediction of the enthalpy of

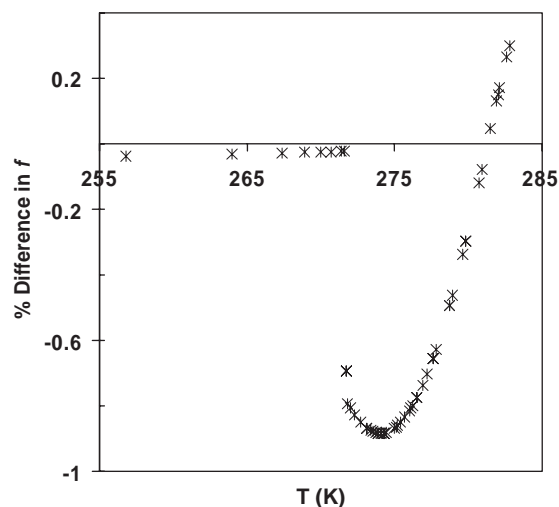


Fig. 5. Percent difference between prediction of the equilibrium fugacity (f) for CO_2 hydrate by Eq. (11) using the parameters in Table 1 when extrapolated to bulk hydrate ($1/r = 0$) and predictions from the SBM. Note that the extrapolations to $1/r = 0$ are based on the parameter values determined from fits obtained in the ranges $2.5 \text{ nm} \leq r \leq 11 \text{ nm}$, and $255 \leq T_f \leq 270$.

dissociation being

$$\Delta H \approx -R \left\{ b + cT_f + \frac{e}{r} + d \left[\frac{(1 + T_0/T_f)(b/T_f + c + e/rT_f) + 1}{(1 + T_0/T_f)^2} \right] \times \exp(a + b/T_f + c \ln(T_0/T_f) + e/rT_f) \right\}. \quad (12)$$

Eq. (12) can be used along with the parameters given in Table 1 to calculate dissociation enthalpies for the hydrates considered in this work. These predictions can then be compared to those resulting from using the full model to perform the same calculations. Table 3 shows the maximum and average errors in using Eq. (12) compared to the full SBM approach. Clearly, the errors are still small, with CO_2 having the largest error of the hydrates considered here.

5. Conclusions

In this work, we have presented explicit relations for the equilibrium fugacities of gas hydrates with a single guest component under bulk conditions, as well as for hydrates in porous media. The first set of such relations showed the dependence of the equilibrium fugacity as well as the enthalpy of dissociation on the classical statistical thermodynamic parameters. The second set of presented relations gave a simpler empirical form which may be useful in applications where the speed and or ease of calculation is imperative. The validity of both sets of relations has been demonstrated for hydrates formed from methane, ethane, CO_2 , and H_2S (sl hydrates), as well as propane (an slI hydrate).

Table 3

Percent differences between hydrate dissociation enthalpies calculated using the SBM and Eq. (12) for several single-component gas hydrates

% Diff in Enthalpy	Methane (sI)	Ethane (sI)	Propane (sII)	Carbon dioxide (sI)	Hydrogen sulfide (sI)
Max abs % diff (liq)	1.11	1.36	1.33	3.29	8.75E – 02
Ave abs % diff (liq)	0.133	0.470	0.081	0.384	4.31E – 02
Max abs % diff (ice)	3.50E – 03	5.58E – 03	1.72E – 02	4.33E – 02	0.176
Ave abs % diff (ice)	4.96E – 04	7.28E – 04	2.03E – 03	4.38E – 03	0.045

Appendix

While Eq. (5) can be solved numerically for the equilibrium pressure by an iterative procedure (given any choice of temperature), it is not possible to solve for the pressure as a function of temperature, explicitly. Our goal is to find an accurate approximation of the true solution that allows such an explicit form to be determined. Previous work (Wilder and Smith, 2002) presented such a solution in the case of gas hydrates where the guest gas solubility in water was negligible, and which had high fractional occupancies of the hydrate cages by guest gas molecules. These approximations have been demonstrated in the current work to be valid for methane, ethane, and propane. For the other gases of interest to us in this work (carbon dioxide and hydrogen sulfide), the fractional occupancy of the hydrate cages is not large enough to allow for the approximations necessary to arrive at Eq. (7). In addition, the solubility of carbon dioxide in water is large enough to necessitate its consideration in the accurate prediction of the equilibrium pressure for hydrates formed by this gas. This appendix presents a new set of approximations which are relevant to these two gas hydrates.

We begin by a consideration of the terms involving either the pressure or fugacity of the gas. The first such term on the left-hand side of Eq. (5) involves the effect of the volume difference between the empty hydrate lattice and the normal state of the water, namely

$$-\int_0^{P_f} \frac{\Delta V_w}{R\bar{T}} dP = -\frac{\Delta V_w}{R\bar{T}} P_f.$$

Due to the relatively small volume change when hydrates form from water, the magnitude of this term is often small compared to others in Eq. (5), and so the error in approximating P by f (the gas fugacity) is small, and so we shall replace

$$-\frac{\Delta V_w}{R\bar{T}} P_f \text{ by } -\frac{\Delta V_w}{R\bar{T}} f.$$

In addition, because of the smallness of this term it can be replaced by $\ln(1 - (\Delta V_w/R\bar{T})f)$ with only the introduction of a very small error. For example, the maximum error in approximating $-(\Delta V_w/R\bar{T})f$ by $\ln(1 - (\Delta V_w/R\bar{T})f)$ for CO₂ hydrate is less than 0.4%. The smallness of this error compounded by the smallness of the original term relative to the others in Eq. (5) makes the overall error negligible.

The next terms in Eq. (5) involving the pressure are those related to the cage occupancies

$$\sum_i \eta_i \ln(1 - Y_i) = \eta_s \ln(1 - Y_s) + \eta_l \ln(1 - Y_l), \quad (\text{A.1})$$

where on the right-hand side we have used a subscript “s” to denote quantities for the “small” cages, and “l” for those in “large” cages. Using the form for Y_i given in Eq. (3), each term of Eq. (A.1) can be rewritten using

$$\begin{aligned} \eta_i \ln(1 - Y_i) &= -\eta_i \ln(1 + C_i f) \\ &= -\eta_i \ln \left[C_i f \left(1 + \frac{1}{C_i f} \right) \right]. \end{aligned} \quad (\text{A.2})$$

Using the results of the above discussion in Eq. (5) leads to (after some algebraic manipulation):

$$\begin{aligned} &\ln \left(f^{(\eta_s + \eta_l)} \left(1 + \frac{1}{C_s f} \right)^{\eta_s} \left(1 + \frac{1}{C_l f} \right)^{\eta_l} (\gamma_w X_w) \right. \\ &\quad \times \left. \left(1 - \frac{\Delta V_w}{R\bar{T}} f \right) \right) \\ &\approx \frac{\Delta \mu_w^0}{RT_0} + \left(\frac{\Delta H_w^0 - T_0 \Delta C_P^0}{R} \right) \left(\frac{1}{T_f} - \frac{1}{T_0} \right) \\ &\quad - \frac{\Delta C_P^0}{R} \ln \left(\frac{T_f}{T_0} \right) - \eta_s \ln(C_s) - \eta_l \ln(C_l) \\ &\quad + V_L \frac{2 \cos(\theta) \sigma}{RT_f r}. \end{aligned} \quad (\text{A.3})$$

Using the relationship between logarithms and exponentials, and then raising both sides to the power $1/(\eta_s + \eta_l)$ yields

$$\begin{aligned} &f \left(1 + \frac{1}{C_s f} \right)^{\frac{\eta_s}{\eta_s + \eta_l}} \left(1 + \frac{1}{C_l f} \right)^{\frac{\eta_l}{\eta_s + \eta_l}} (\gamma_w X_w)^{\frac{1}{\eta_s + \eta_l}} \left(1 - \frac{\Delta V_w}{R\bar{T}} f \right)^{\frac{1}{\eta_s + \eta_l}} \\ &\approx \frac{\left(\frac{T_0}{T_f} \right)^{\frac{\Delta C_P^0}{R(\eta_s + \eta_l)}} \exp \left(\frac{\Delta \mu_w^0}{RT_0} + \left(\frac{\Delta H_w^0 - T_0 \Delta C_P^0}{R} \right) \left(\frac{1}{T_f} - \frac{1}{T_0} \right) + V_L \frac{2 \cos(\theta) \sigma}{RT_f r} \right)}{C_s^{\frac{\eta_s}{(\eta_s + \eta_l)}} C_l^{\frac{\eta_l}{(\eta_s + \eta_l)}}} \equiv a(T). \end{aligned} \quad (\text{A.4})$$

While for many gases it is possible to neglect their solubility in water, for those with moderate solubility (such as carbon dioxide) this leads to a significant error in the approximation of the hydrate equilibrium pressure (or fugacity). Following the approach of Munck et al. (1988) we shall approximate the term related to the solubility of carbon dioxide in water by $\gamma_w X_w = 1 - X_{\text{CO}_2}$. The mole fraction of CO_2 in the aqueous phase is calculated based on the parameters for the Henry's law constant (h_w) as a function of temperature as given by Munck. Thus, the solubility term becomes (Munck et al., 1988)

$$\gamma_w X_w = 1 - X_{\text{CO}_2} = 1 - \frac{f e^{-P\bar{V}/RT}}{h_w}, \quad (\text{A.5})$$

with $h_w = \exp(A + B/T + C \ln T + DT)$. Due to the small magnitude of the argument of the exponential in the above

the resulting product retaining only terms that are quadratic (or less) in the gas fugacity leads to (after some algebraic simplification):

$$\begin{aligned} & \frac{1}{\eta h_w} \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1-\eta}{2h_w} \right) \right) f^2 \\ & - \left(\frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1}{h_w} \right) - 1 \right) f \\ & + \left(a(T) - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \right) \approx 0, \end{aligned} \quad (\text{A.7})$$

where $\eta = \eta_s + \eta_l$. While use of the quadratic formula to solve (A.7) yields two solutions, only the smaller solution is physically realistic (the other is a so-called extraneous root introduced due to the solution procedure, and results in a contradiction when used in the original equation). Thus, we arrive at

$$\begin{aligned} f \approx & \frac{\eta h_w \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1}{h_w} \right) \right)}{2 \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1-\eta}{2h_w} \right) \right)} \\ & \times \left(1 - \sqrt{1 - \frac{4 \left(a(T) - \frac{1}{\eta} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \right) \left(1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1-\eta}{2h_w} \right) \right)}{\eta h_w \left(\frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \left(\frac{\Delta V_w}{R\bar{T}} + \frac{1}{h_w} \right) - 1 \right)^2}} \right). \end{aligned} \quad (\text{A.8})$$

equation for carbon dioxide, we can approximate Eq. (A.5) by $\gamma_w X_w \approx 1 - \frac{f}{h_w}$. Using this in Eq. (A.4) yields

$$\begin{aligned} & f \left(1 + \frac{1}{C_s f} \right)^{\frac{\eta_s}{\eta_s + \eta_l}} \left(1 + \frac{1}{C_l f} \right)^{\frac{\eta_l}{\eta_s + \eta_l}} \\ & \times \left(1 - \frac{f}{h_w} \right)^{\frac{1}{\eta_s + \eta_l}} \left(1 - \frac{\Delta V_w}{R\bar{T}} f \right)^{\frac{1}{\eta_s + \eta_l}} \approx a(T), \end{aligned} \quad (\text{A.6})$$

where $a(T)$ is as defined in Eq. (A.4). Note that each of the binomial terms on the left of Eq. (A.5) involves unity plus or minus a small quantity, all raised to a power. Examination of the individual terms shows that each is well approximated by keeping only the first two terms of the corresponding Taylor series, except for the term resulting from the

We note that Eq. (A.8) is independent of the method by which the Langmuir constants (the C_i s) are calculated. For the purposes of this work we shall use the form given in Eq. (4).

The enthalpy of dissociation of single guest hydrates can be predicted through the use of Eq. (6). Rearranging Eq. (6) and using the identity that

$$\frac{d(\ln(f))}{dz} = \frac{1}{f} \frac{\partial f}{\partial z}$$

leads to

$$\Delta H = -R \frac{d(\ln(f))}{d(1/T)} = -R \frac{1}{f} \frac{\partial f}{\partial (1/T)}. \quad (\text{A.9})$$

Differentiating Eq. (5) with respect to $1/T$ (after making the replacement of P by f in the term involving the volume difference between the empty hydrate lattice and the normal state of the water, as was discussed above), one finds

$$\frac{\partial f}{\partial (1/T)} \approx \frac{\frac{1}{R} (\Delta H_w^0 + (T_f - T_0) \Delta C_P^0 + V_L 2 \cos(\theta) \sigma_r^{\frac{1}{r}}) - \left(\frac{\eta_s C'_s}{1 + C_s f} + \frac{\eta_l C'_l}{1 + C_l f} - \frac{h'_w}{h_w^2} - \frac{\Delta V_w}{2R} \left(\frac{T_f}{\bar{T}} \right)^2 \right) f}{\frac{\eta_s C_s}{1 + C_s f} + \frac{\eta_l C_l}{1 + C_l f} - \frac{1}{h_w f} - \frac{\Delta V_w}{R\bar{T}}}, \quad (\text{A.10})$$

effects of solubility, which requires the retention of the first three terms. Performing these expansions, and computing

where the form of the Langmuir and Henry's Law constants used by Munck et al. (1988) lead to their derivatives with

respect to $1/T$ being given by

$$\frac{d(C_i)}{d(1/T)} = C'_i = (T + B_i)C_i$$

and

$$\frac{d(h_w)}{d(1/T)} = h'_w = (B - CT - DT^2)h_w.$$

Eqs. (A.8)–(A.10) can now be used together to calculate the enthalpy of dissociation based on the approximations given in this work. For cases where the gas solubility in water is negligible, but where one still needs to account for fractional occupancies that are not large enough to allow for the use of Eqs. (7), (7b) is replaced by

$$f \approx \frac{a(T) - \frac{1}{\eta} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right)}{1 - \frac{1}{\eta^2} \left(\frac{\eta_s}{C_s} + \frac{\eta_l}{C_l} \right) \frac{\Delta V_w}{RT}} \quad (\text{A.11})$$

and the term involving the Henry's Law constant in Eq. (A.10) is neglected when computing the enthalpy. We note that any of the above Eqs. (A.7), (A.10) or (A.11) can be applied to hydrates involving guests which only occupy the large cages by setting η_s equal to zero (and therefore $\eta = \eta_l$).

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